“Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania”

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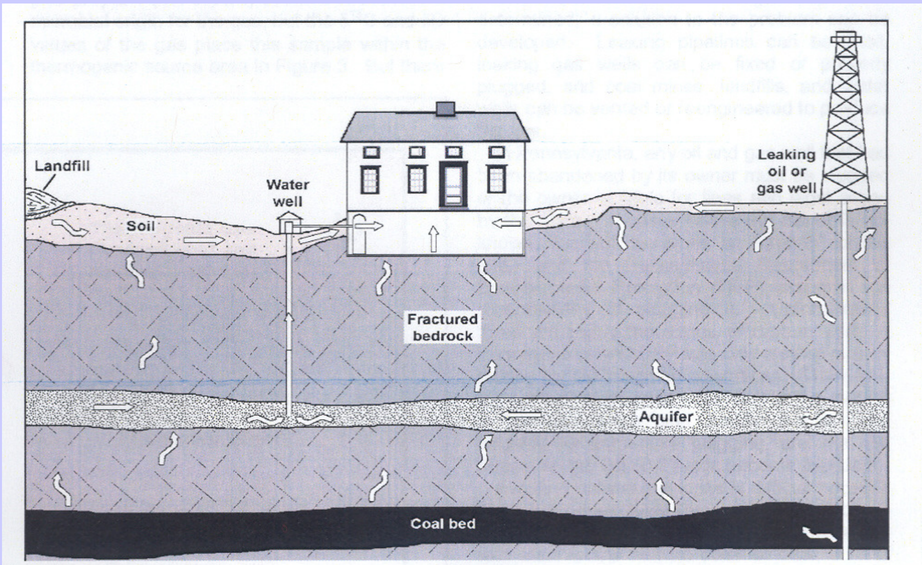
Stray Gas Workshop
Pittsburgh Geological Society
November 3-6, 2009.

USGS

In cooperation with PADEP (Pennsylvania Department of Environmental Protection)

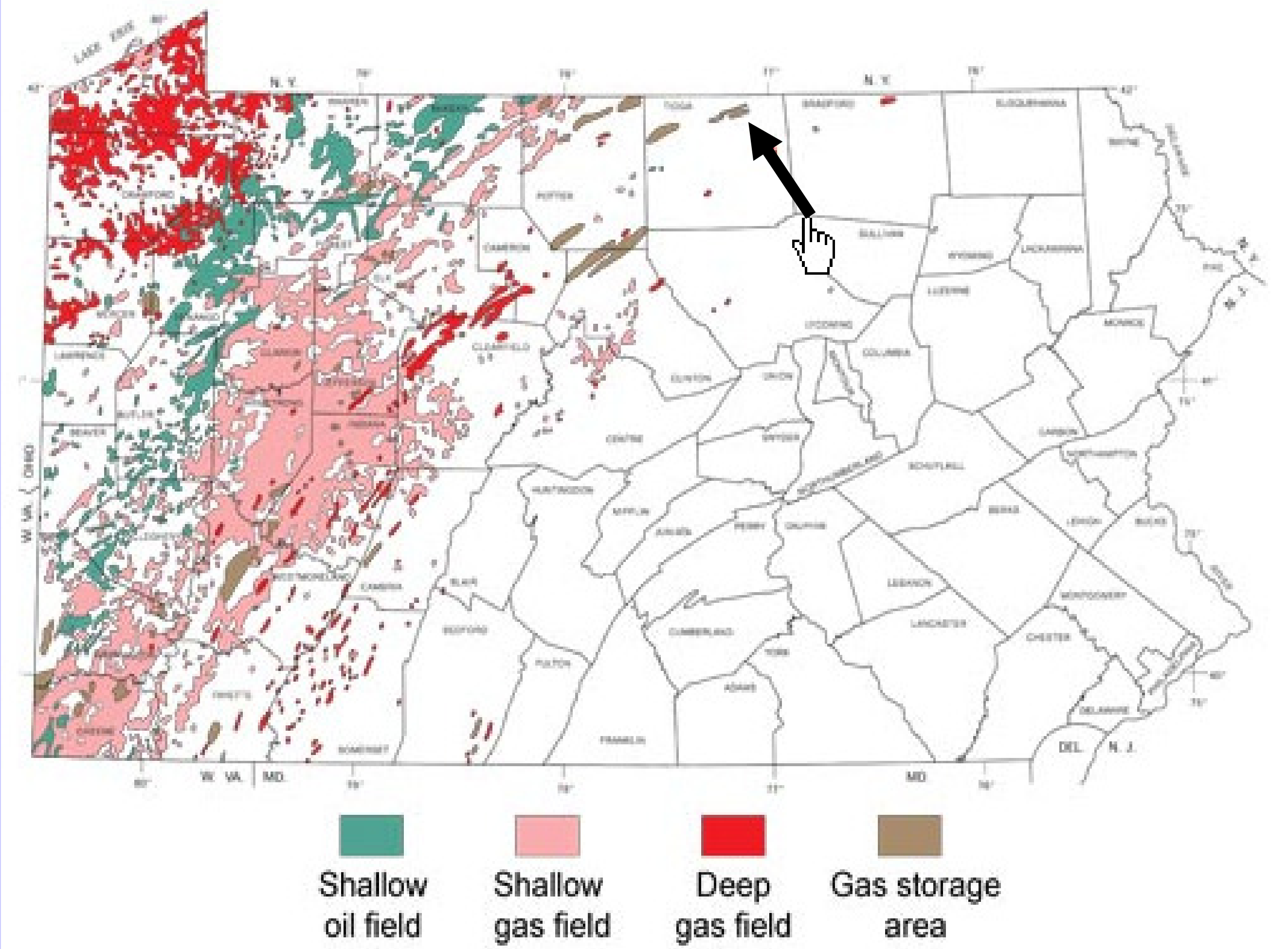
Natural Gas Migration Problem in Pennsylvania



The Pittsburgh Geological Society

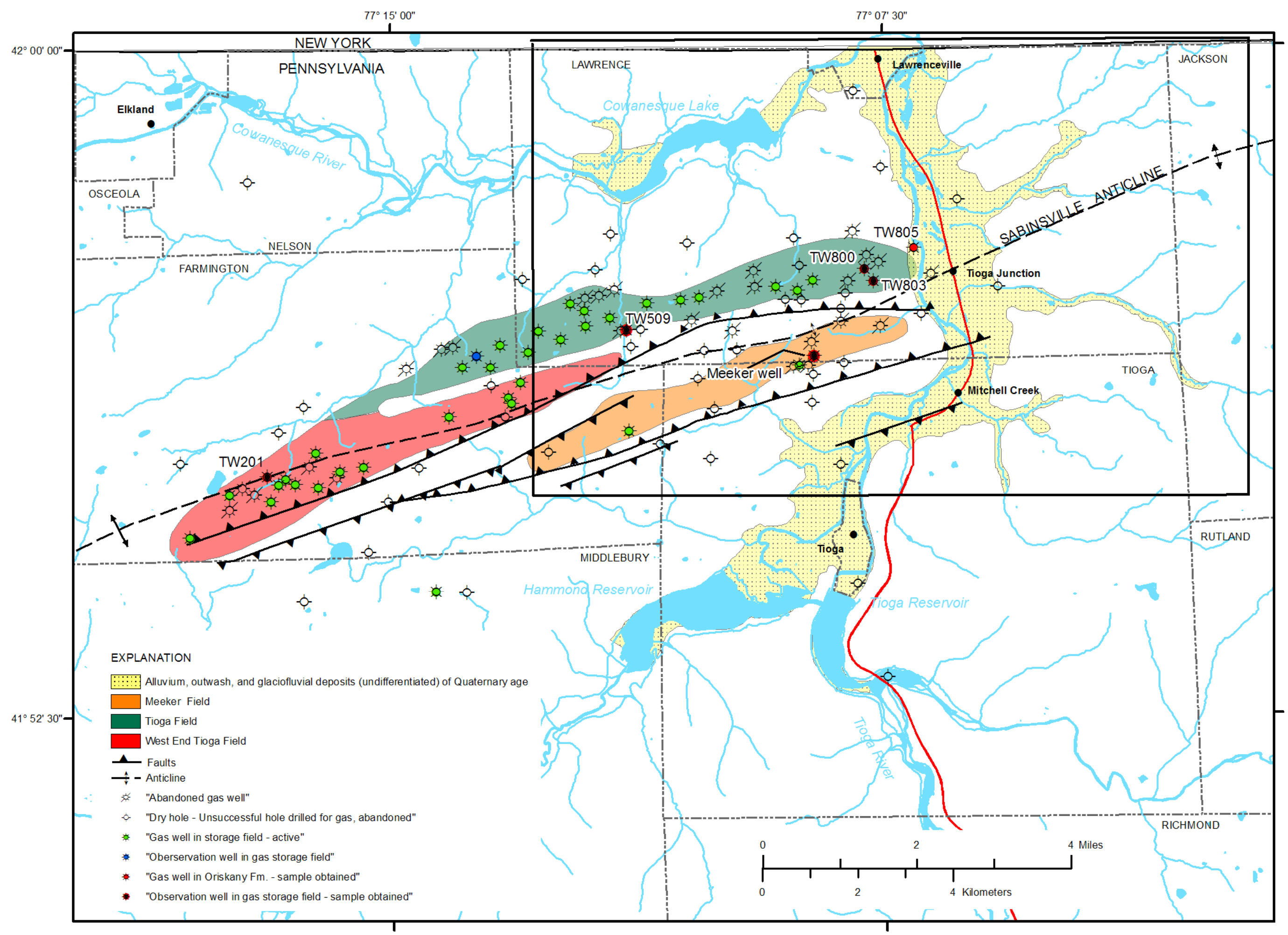
Northeastern United States of America

Tioga Junction Study Area –Tioga Gas-Storage Field



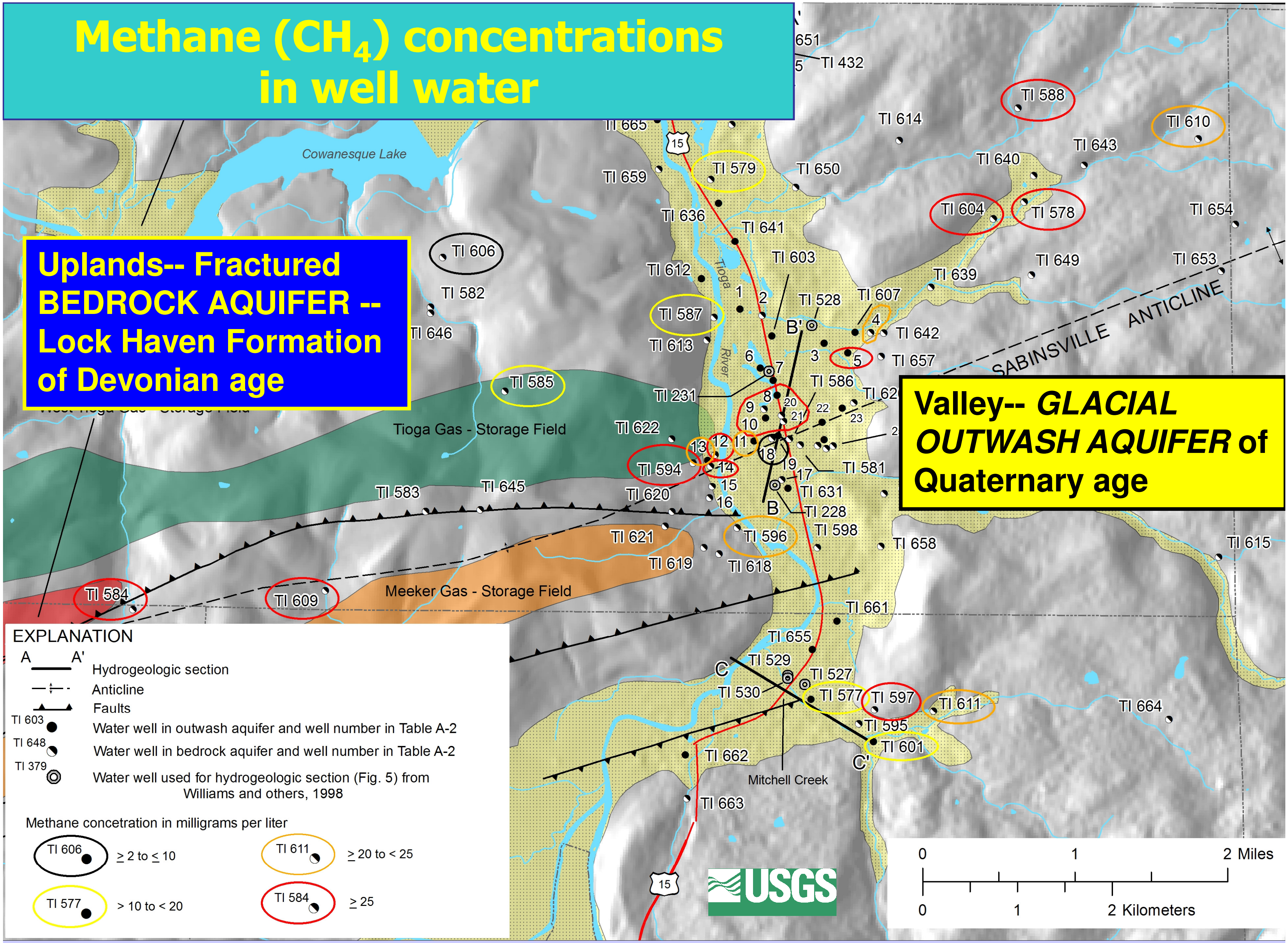
GAS-STORAGE FIELDS & MAJOR GEOLOGIC STRUCTURES

Storage fields are 3,500 - 4,100 feet below surface in Devonian rock.



USGS

Methane (CH_4) concentrations in well water



Delta notation

$$\delta^{13}\mathrm{C} = \frac{R_{sample} - R_{reference}}{R_{reference}}$$

Where R = $^{13}C/^{12}C$,
$R_{reference}$= VPDB (Vienna Pee Dee Belemnite)

$$\delta^{13}\mathrm{C} = \delta\left(^{13}\mathrm{C}\right) = \delta\left(^{13}\mathrm{C}/^{12}\mathrm{C}\right) = \frac{n_{\mathrm{X}}\left(^{13}\mathrm{C}\right)/n_{\mathrm{X}}\left(^{12}\mathrm{C}\right) - n_{\mathrm{ref}}\left(^{13}\mathrm{C}\right)/n_{\mathrm{ref}}\left(^{12}\mathrm{C}\right)}{n_{\mathrm{ref}}\left(^{13}\mathrm{C}\right)/n_{\mathrm{ref}}\left(^{12}\mathrm{C}\right)}$$

Microbial Methane production

1. Near-surface environment, marsh etc.

CH_4 production by fermentation pathway:

$CH_3COOH = CH_4 + CO_2$

Isotope change: Intra-molecular fractionation: $CH_3 = \delta^{13}C$ in CH_3 depleted; $\delta^{13}C$ in COOH is enriched.

Product: $CH_4 = \delta^{13}C$ depleted; $CO_2 = \delta^{13}C$ enriched. (DIC)

Concentration change: CH_3COOH decreasing

CH_4 and CO_2 increasing (DIC)

2. Drift gas -old, covered by glacial drift deposit.

CH_4 production by CO_2 reduction pathway :

$CO_2 + 4H_2 = CH_4 + 2H_2O$

Isotope change: $CH_4 = \delta^{13}C$ depleted; $CO_2 = \delta^{13}C$ enriched (DIC);

Concentration change: CH_4 increasing, CO_2 decreasing (DIC)

3. Minimal C_2 and C_3 production, $\delta^{13}C$ = very depleted in ^{13}C.

USGS

Thermogenic Methane production

– formed by thermal break down.

Higher hydrocarbon (C_2; C_3; etc.) present

$\delta^{13}C$ isotope of CH_4 is closer to the isotope of substrate it is produced from (more enriched than microbial). $\delta^{13}C$ of C_2 and C_3 are more enriched than microbial.

Methane oxidation

independent from production pathways

$$2CH_4 + 4O_2 = 2CO_2 + 4H_2O$$

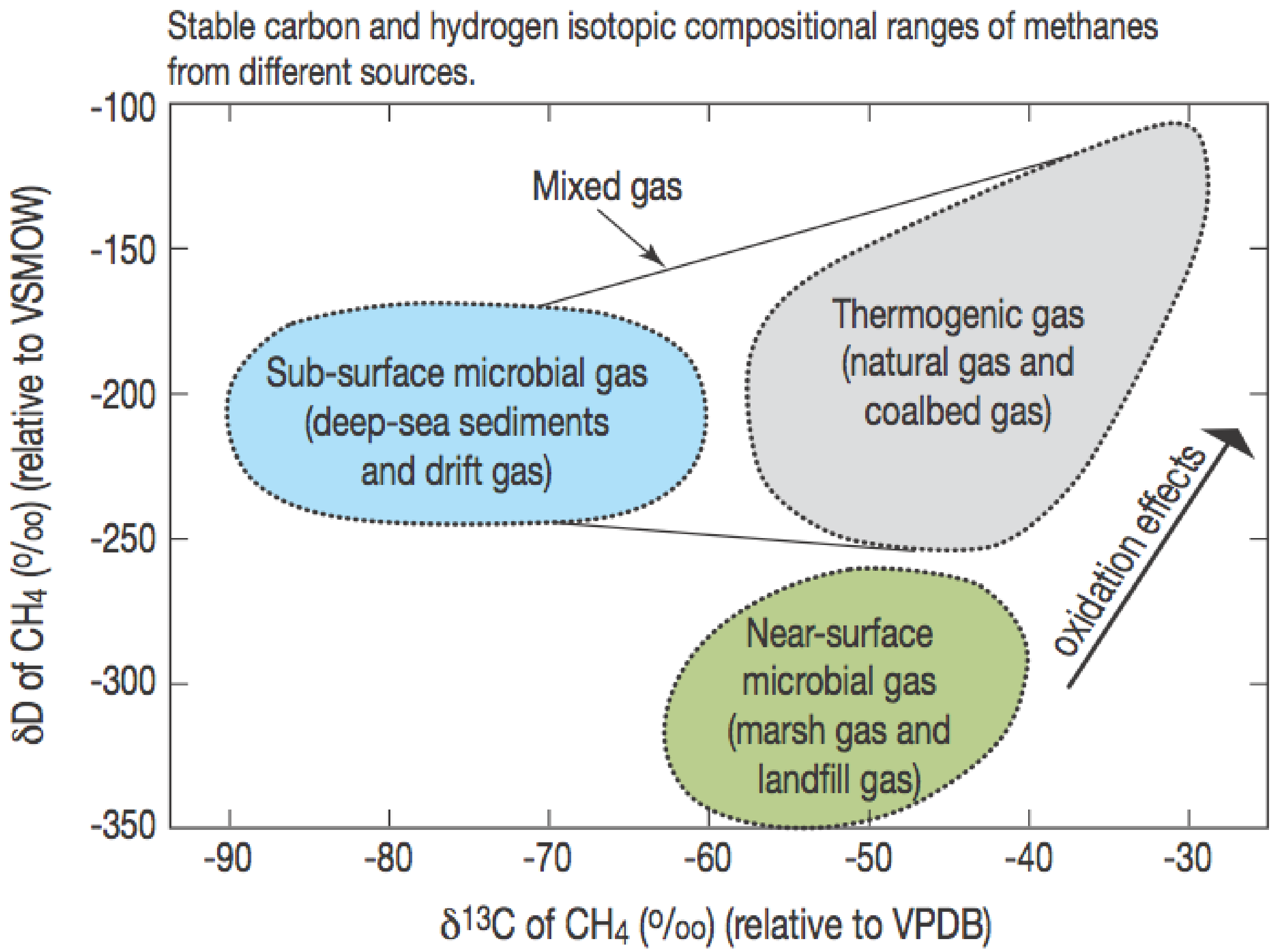
Concentration change:

CH_4 decreasing, CO_2 (DIC) increasing.

δ^{13}C isotope change:

CH_4 becomes enriched ; CO_2 (DIC) becomes depleted

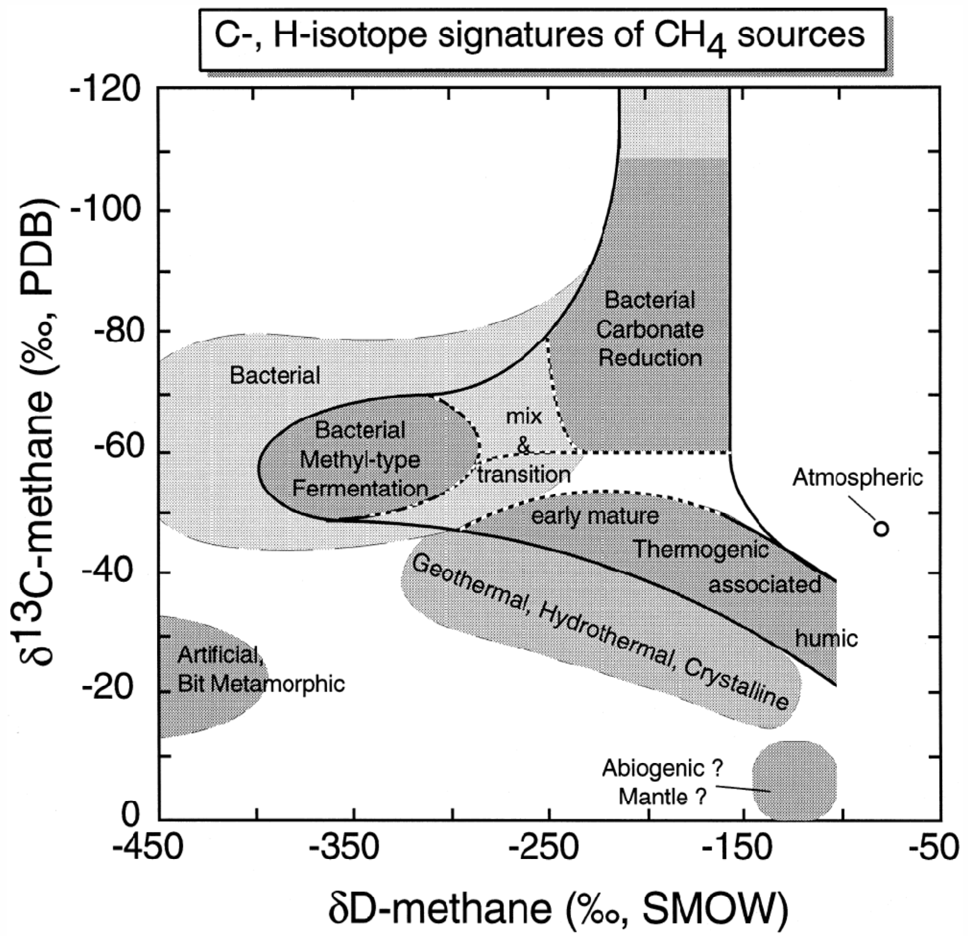
Stable Isotope ranges of methanes from different sources



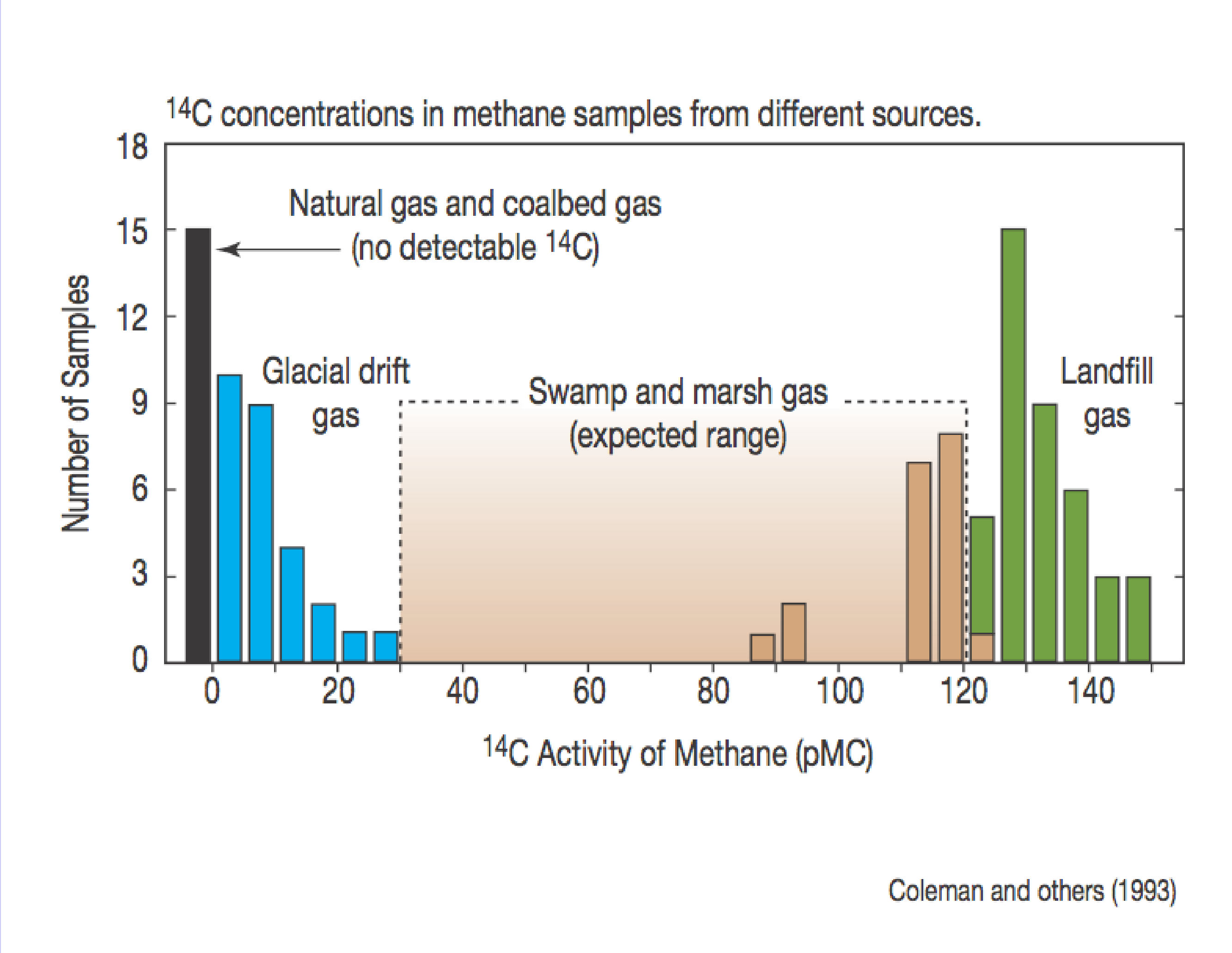
After Coleman and others (1993) based on the data set of Schoell (1980)

Whiticar, 1999:
Thermogenic Gas:
$\delta^{13}C$=-50 to -20‰;
δD= -275 to-100‰
Microbial Gas:
$\delta^{13}C$=-80 to-50‰;
δD=-400 to -300‰
$\delta^{13}C$=-50 to-20‰;
δD=-350 to -100‰

Stable Isotope ranges of methanes from different sources (Whiticar, 1999)



^{14}C pMC (percent modern carbon) in methane from different sources



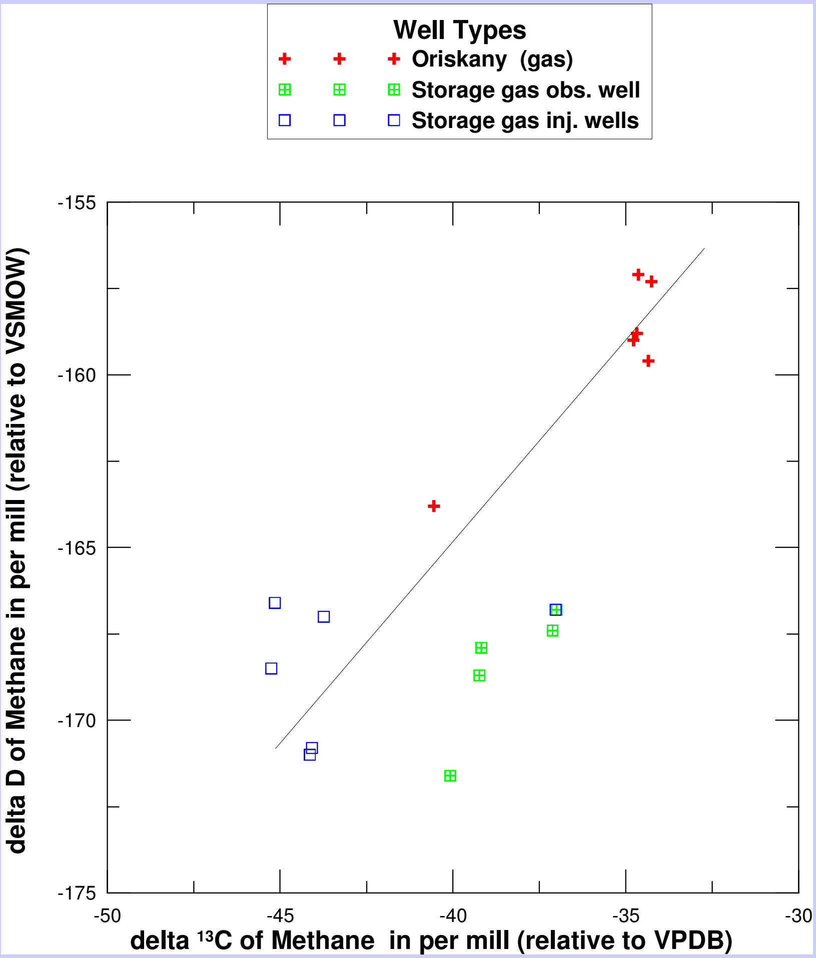
Possible Origins of Methane in the Area

- **Oriskany gas** - *thermogenic*, used up long time ago.
- **Pipe Line gas** – *thermogenic.*
- *Microbial* from possible landfill, or natural decay of organic matter.
- *Devonian gas* (shallow) - *thermogenic*.
- **Mixture** of all above.

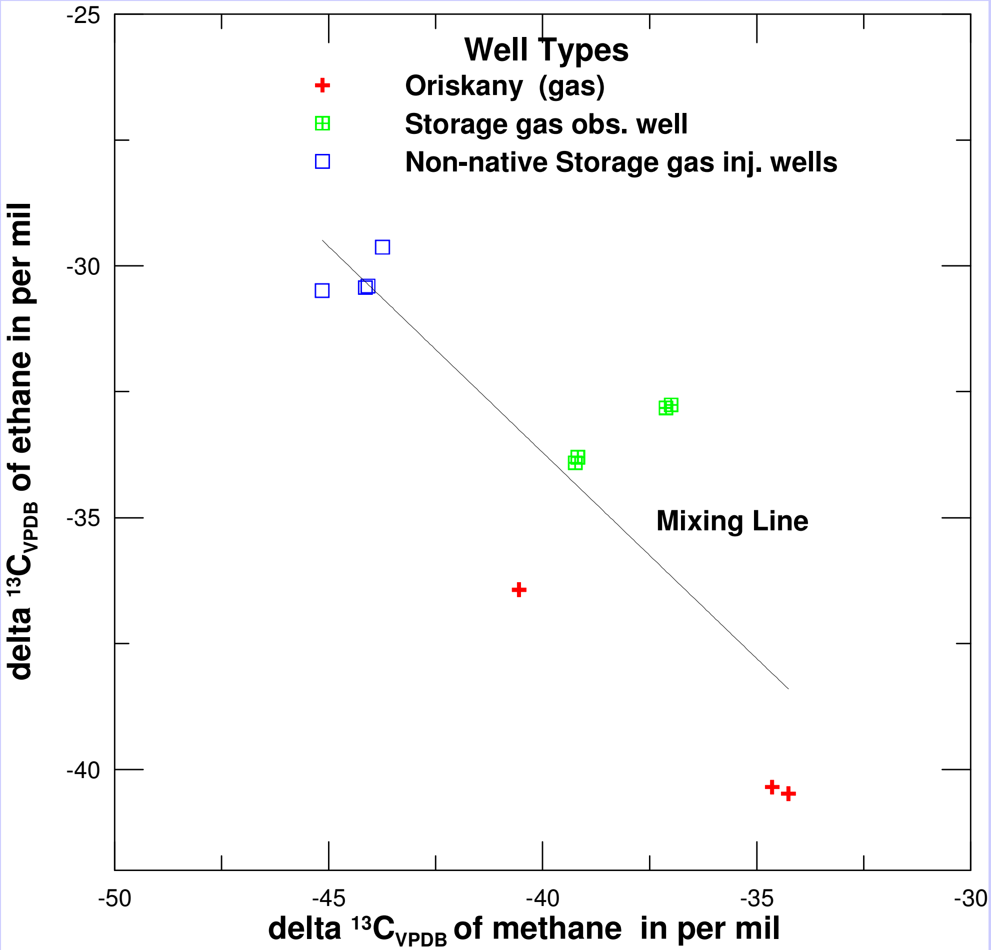
Sample collection and analyses

- **Collections:**
  - End member Gases: Oriskany, Pipe Line; Storage gas.
  - Groundwater, containing methane (C1).
- **Analysis:**
  - ^{13}C of C1 and C2; Deuterium of C1; ^{14}C of C1 of some samples, Dissolved gas concentration, Water isotopes, ^{13}C of DIC, Alkalinity.

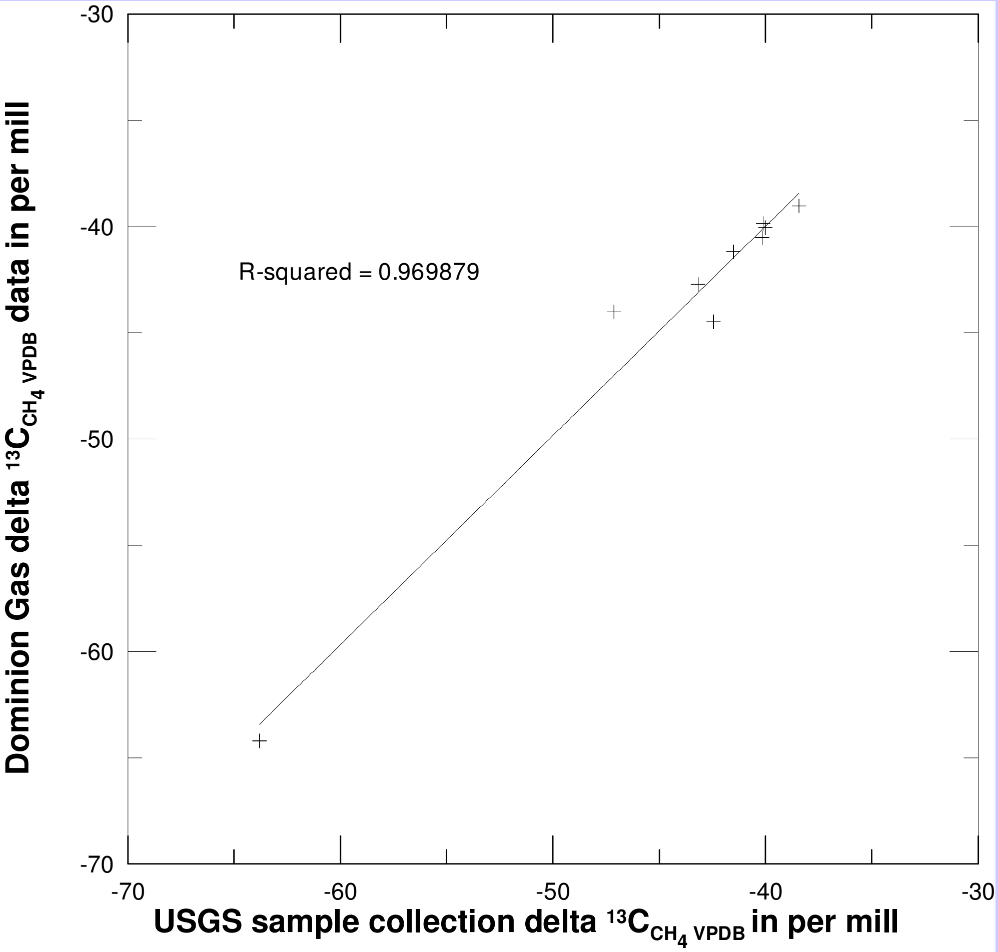
$\delta^{13}C$ and δD of CH_4 in sampled end members of natural gas



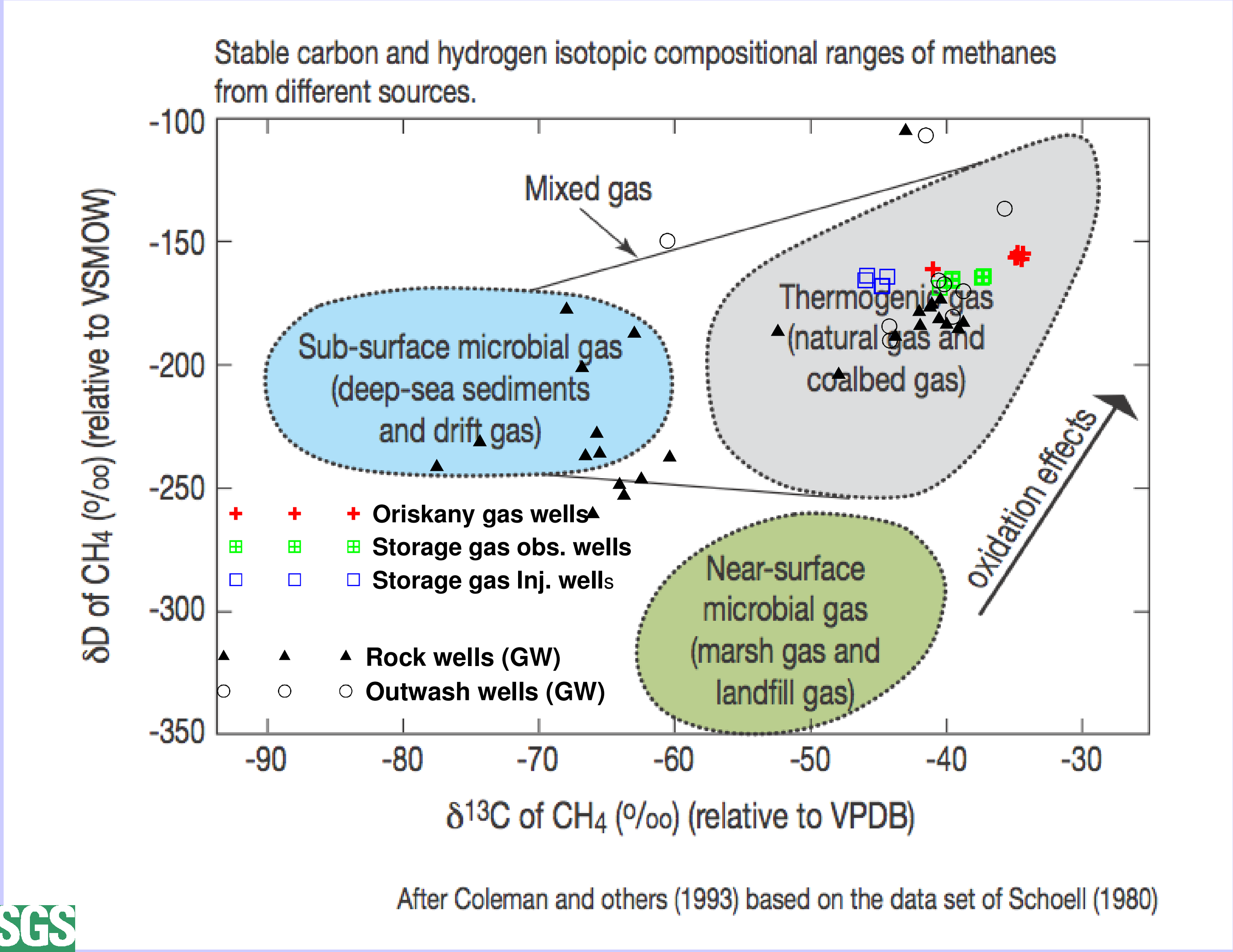
$\delta^{13}C$ of CH_4 and C_2H_6 in end member gas wells

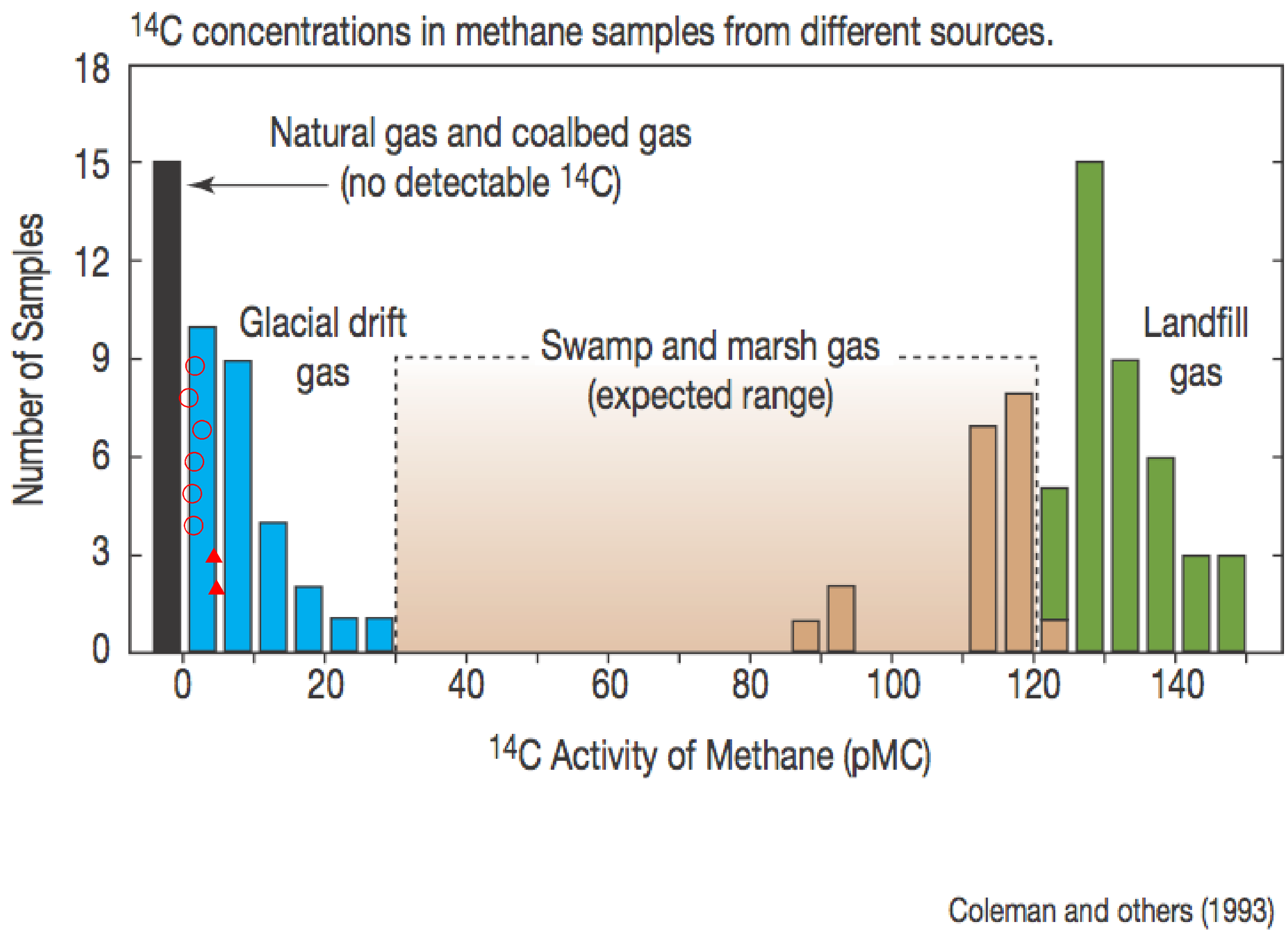


$\delta^{13}C$ of CH_4, collected by USGS and Dominion Gas Co.



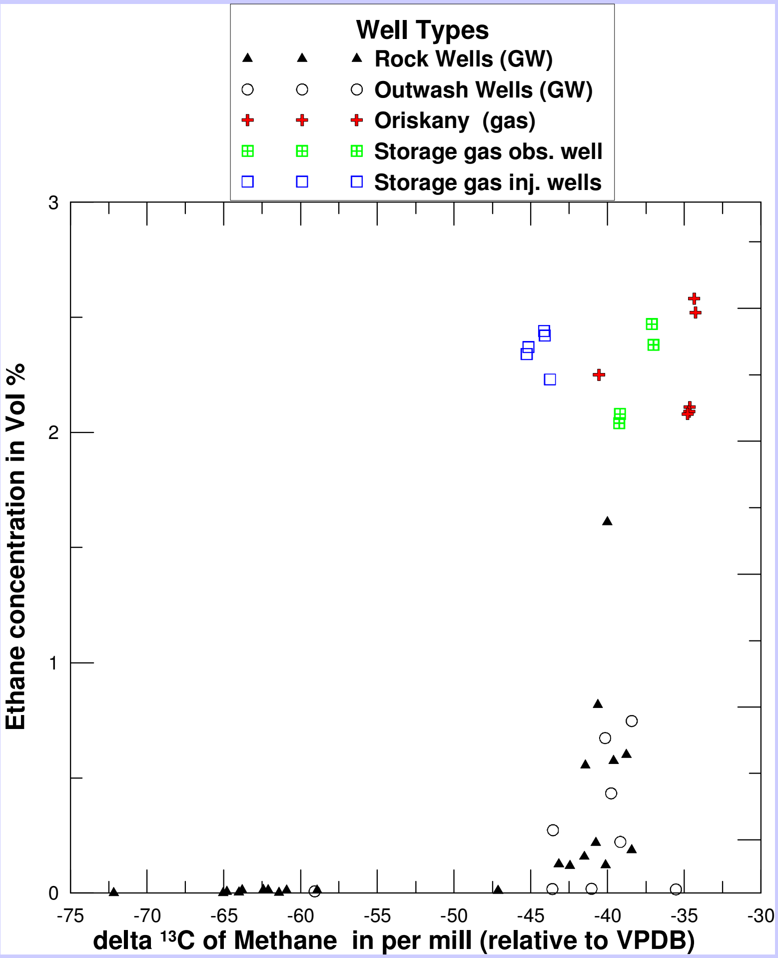
Whiticar, 1999:
Thermogenic Gas: δ¹³C=-50 to -20‰; δD= -275to -100‰
Microbial Gas:δ13C=-110 to -50‰; δD= -400 to -150‰



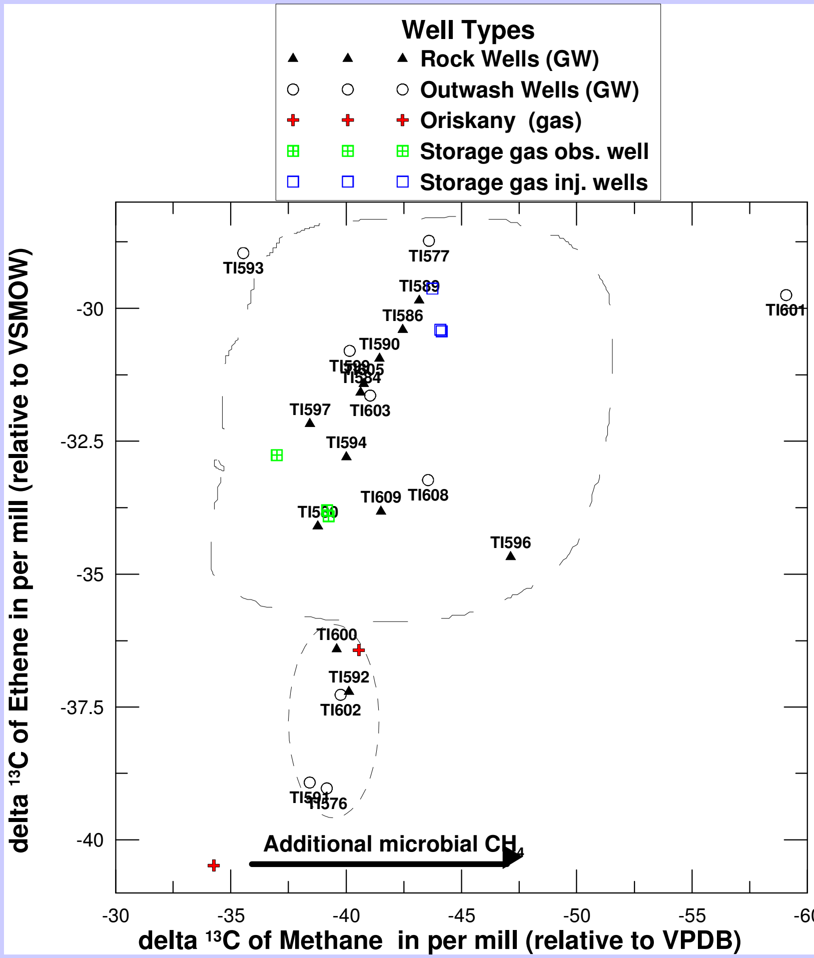


14C concentrations in methane samples from different sources.
Natural gas and coalbed gas
(no detectable 14C)
Glacial drift gas
Swamp and marsh gas
(expected range)
Landfill gas
Number of Samples
0
3
6
9
12
15
18
0
20
40
60
80
100
120
140
14C Activity of Methane (pMC)
Coleman and others (1993)

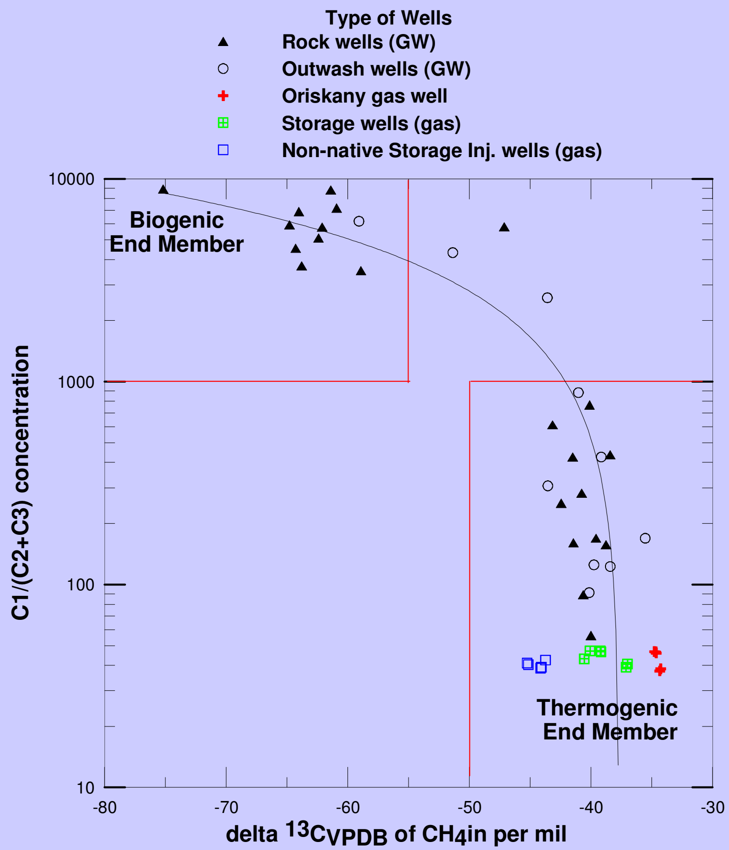
Relationship between ^{13}C of CH_4 and conc. of C_2H_6 in wells



$\delta^{13}C$ of CH_4 and C_2H_6 for gas and ground-water (GW) samples

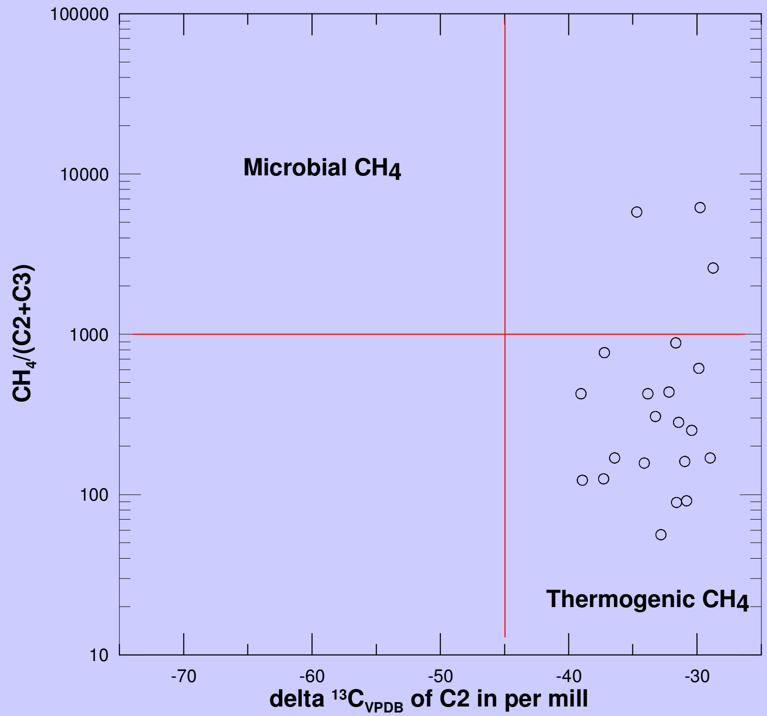


Bernard Graph
Bernard and others 1976

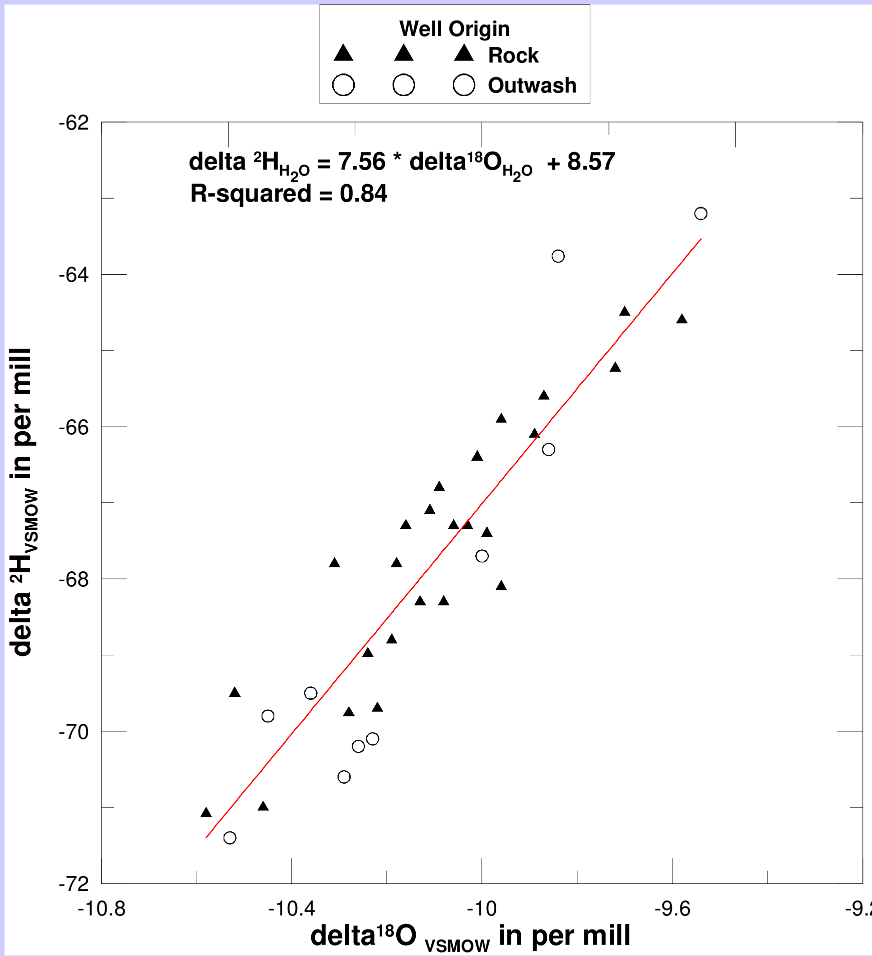


Modified Bernard Graph

Taylor and others, 2000

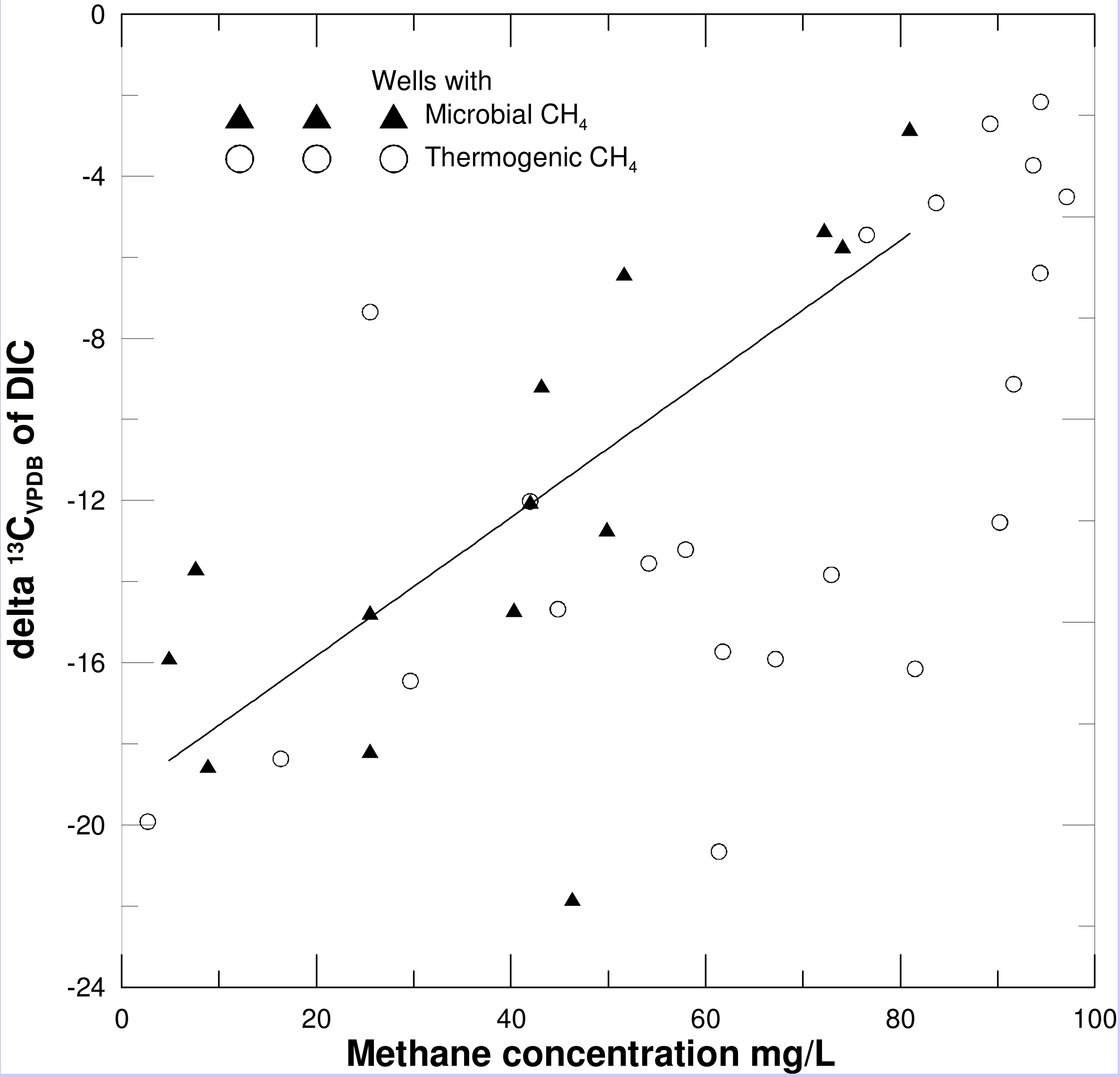


Meteoric Water Line in GW



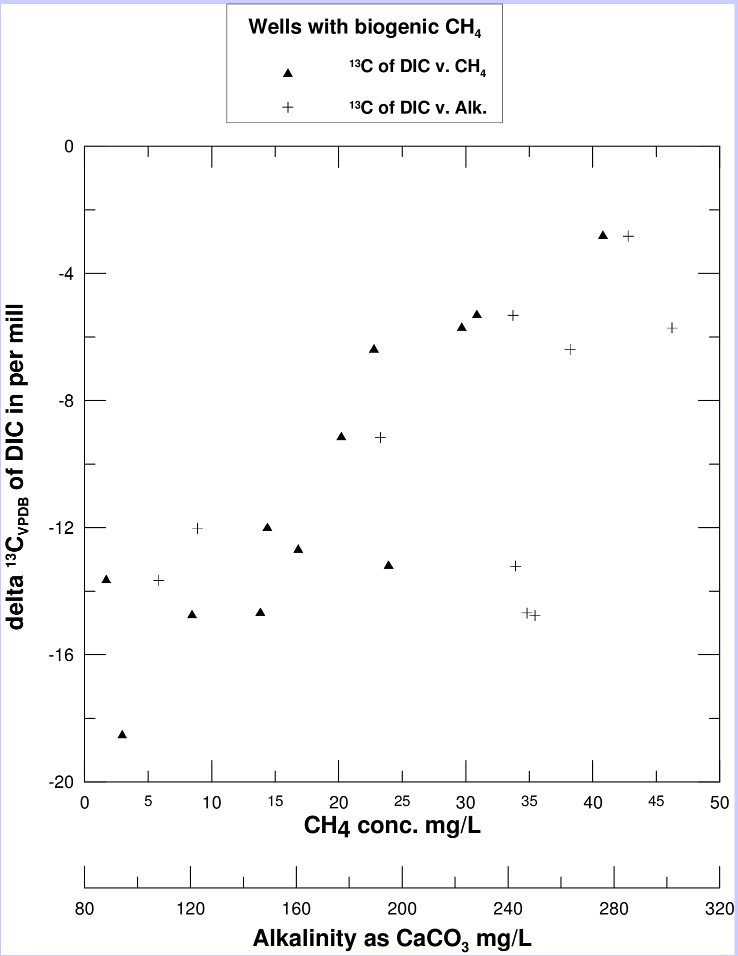
All GW data fall on the same MW-line.

Relationship between CH_4 and coexisting water



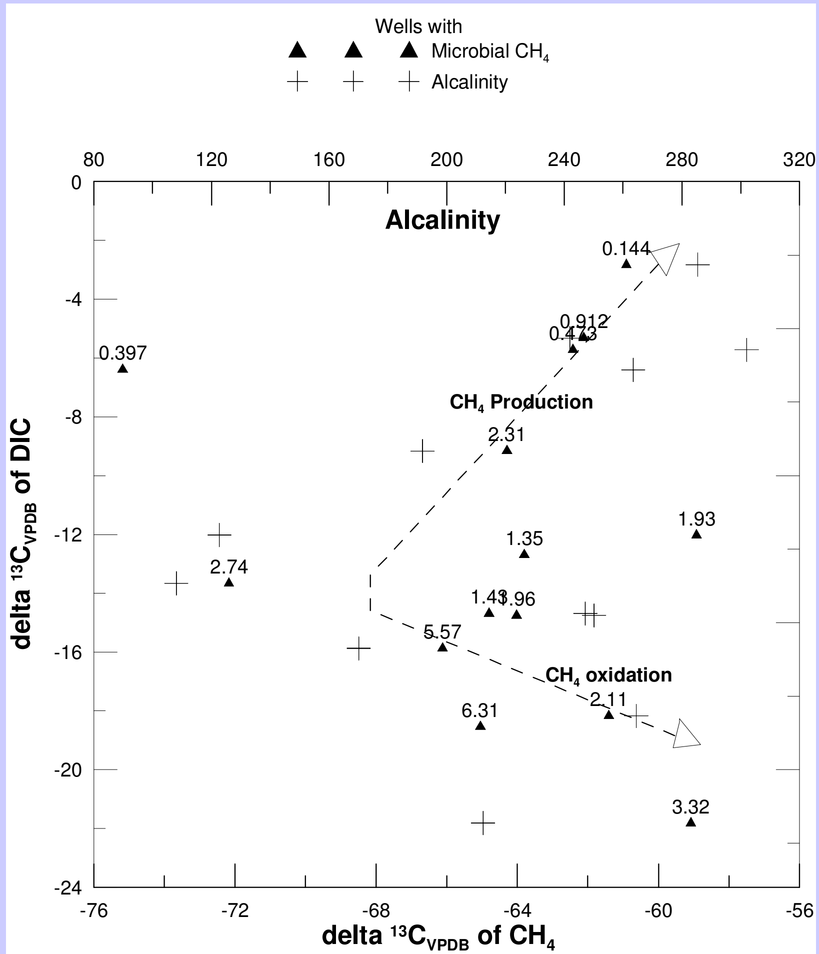
What else could make the DIC -4‰ than CH4 production? Background is around -14 ‰.

Relationship between microbial CH_4 and coexisting water



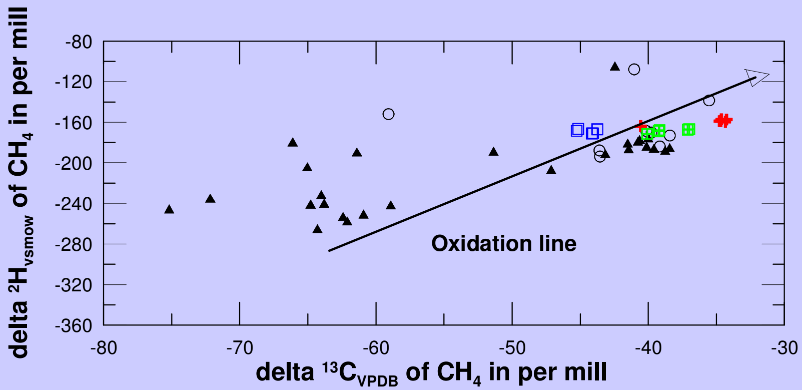
This indicate a CH_4 production; the higher the DIC conc. the more enriched in ^{13}C isotope.
In case of CH_4 oxidation depleted ^{13}C-of DIC should correlate with higher conc. of DIC.

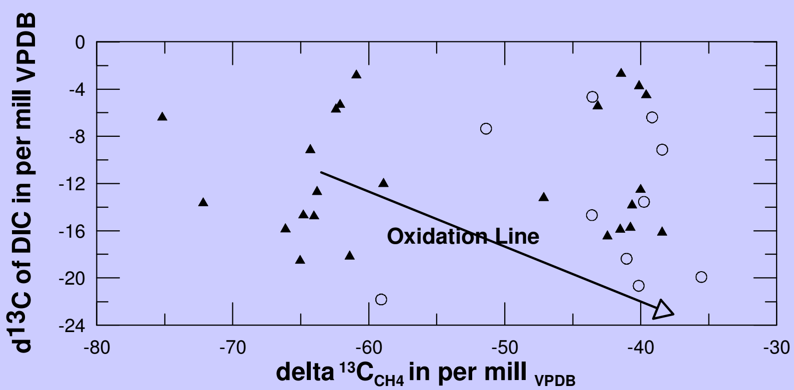
Microbial Methane production and Consumption (Whiticar, 1999)



This indicate an acetate fermentation pathway CH_4 production; DIC conc.is increasing, and its isotope is enriched in C-13. There could be CH_4 oxidation as well, where DIC conc. increasing, its ^{13}C is depleted, CH4 conc. decreasing, ^{13}C of CH_4 is enriched.

$\delta^{13}C$ and $\delta^{2}H(\delta D)$ of CH4 and $\delta^{13}C$ of DIC in sampled water wells





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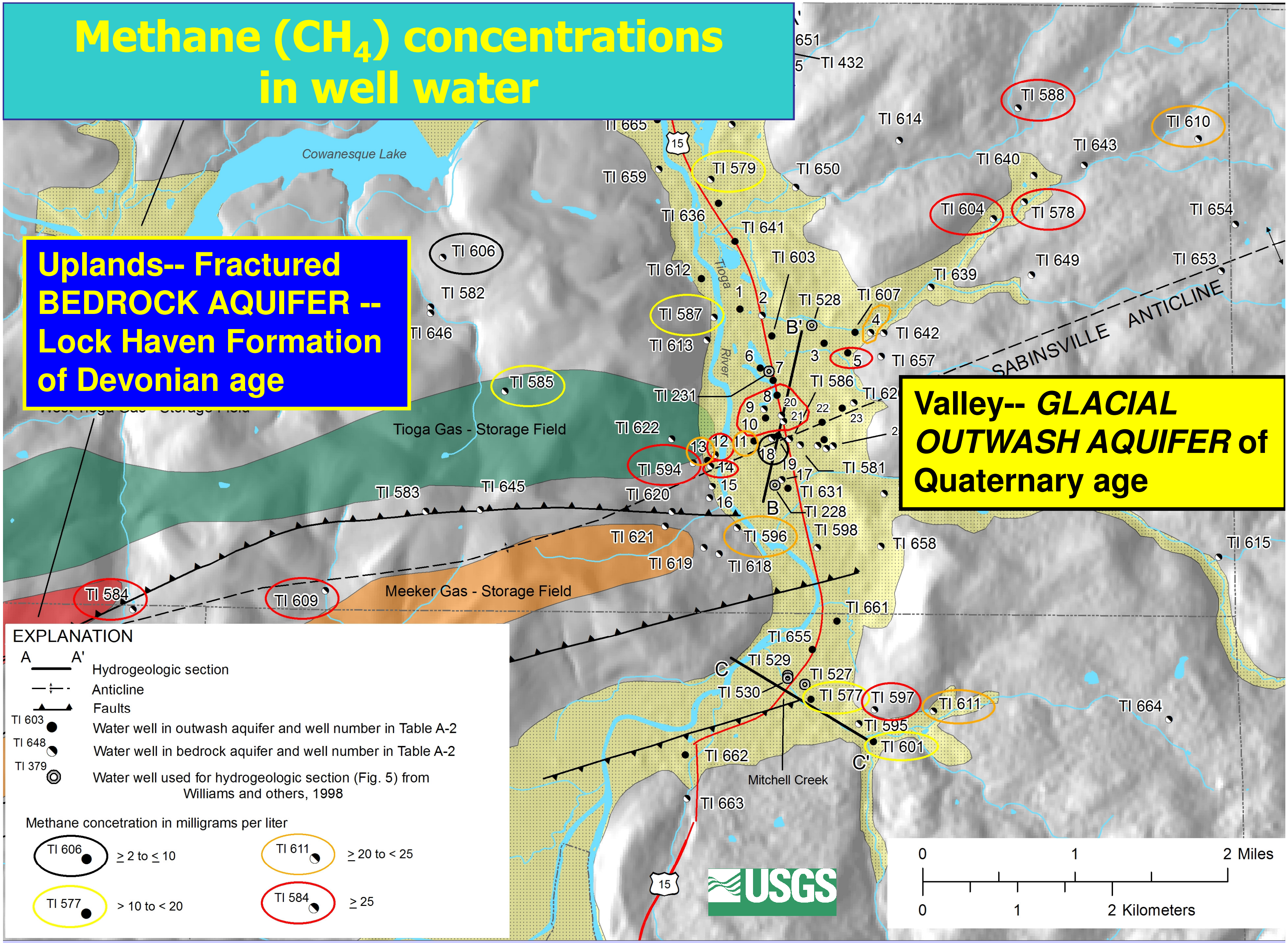
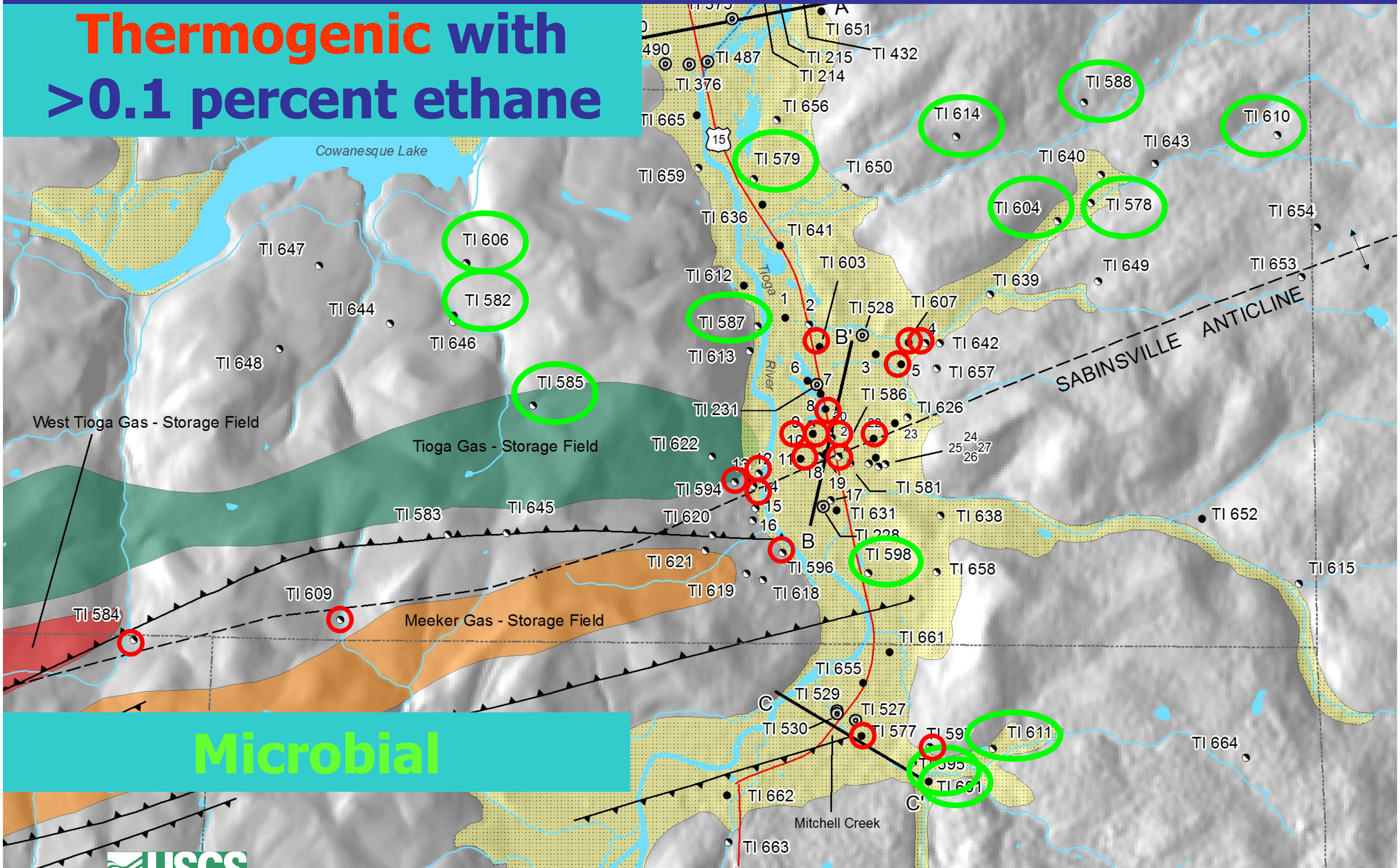


Methane Signatures in Groundwater from Wells



Acknowledgments

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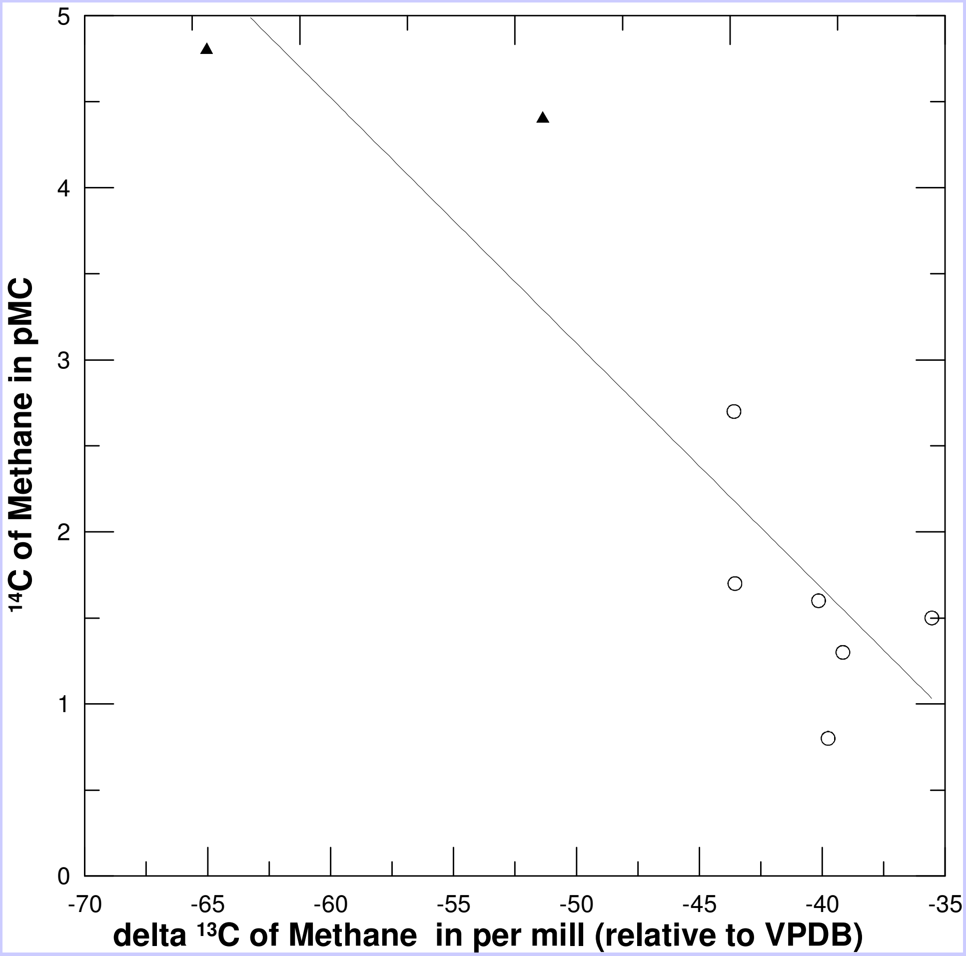
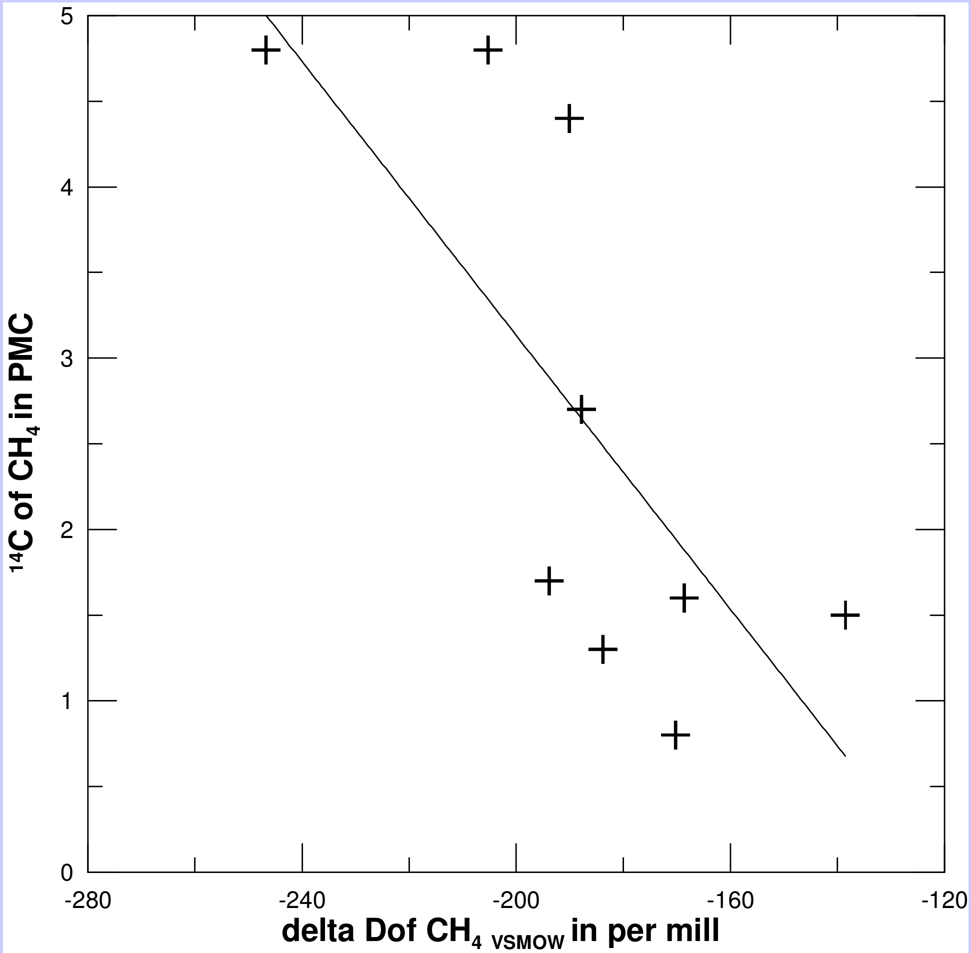
- Reviewers:
  - Dennis Coleman from ISOTECH Lab.
  - Allan Kolker and Curtis Schreffler from USGS.
  - R.C. Burruss from USGS.
  - One unoynimous reviewer.

USGS

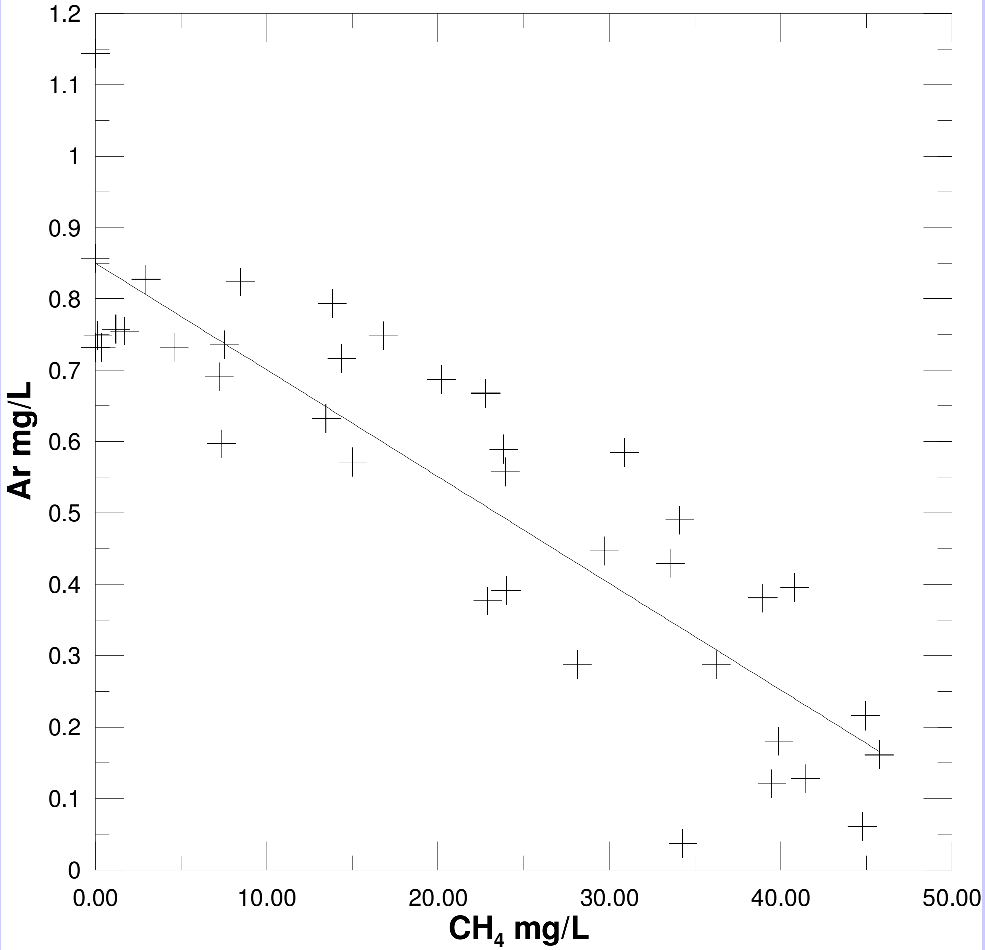
Relation ship between ^{14}C and ^{13}C isotopes of CH_4 in GW wells



Relation ship between ^{14}C and D isotopes of CH_4 in GW wells



Relationship of Ar and Methane concentration in water wells



Solubility of gases at 15 oC
Ar = 0.07 g/kg
CH4= 0. 028 g/kg
C2H6 = 0.08 g/kg